Final Technical Report
"Ion Dynamics Related to Hypersonics"

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I. Introduction, Publications and Personnel

With AFOSR support over several grant cycles, we have developed new approaches to obtaining detailed information on ion-neutral processes, many of which have atmospheric relevance. For example, we coupled infrared chemiluminescence[1-3] and laser-induced fluorescence[4-6] detection with flowing afterglow instrumentation for the first time and characterized the energy disposal (product states)[7,8] for a wide variety of ion-molecule reactions. We studied rate coefficients of reactions[9] and electronic emissions,[10,11] as well as deactivation processes[12,13] and reactions[14-16] of vibrationally state-selected reactant ions. We developed novel experiments to probe the microscopic basis of mobility and alignment using state selective and frequency-resolved laser Doppler probing of ions in drift tubes.[17-20] We measured the mobilities of many atmospheric cluster ions[21-23] and aromatic ions[24] for the first time. Recently we developed a new series of experiments using ultrafast soft x-rays and ultraviolet high order harmonics[25] to probe the photoelectron spectra of chemically interesting neutral species. In the Publications list here, we include all the recent AFOSR sponsored work, from the ongoing ion projects through the new ultrafast soft x-ray project. In the Final Technical Report below, we describe our recent work[26-32] on ion dynamics related to hypersonics.

Publications Sponsored by AFOSR 1996-present

S. Kato, J. A. de Gouw, C.-D. Lin, V. M. Bierbaum, and S. R. Leone, "Vibrational enhancement of the charge transfer rate constant of N_2^+(v=0-4) with Kr at thermal energies," J. Chem. Phys. **105**, 5455 (1996).

S. Kato, J. A. de Gouw, C.-D. Lin, V. M. Bierbaum, and S. R. Leone, "Charge transfer rate constants for N_2^+ (v=0-4) with Ar at thermal energies," Chem. Phys. Lett. **256**, 305 (1996).

M. Krishnamurthy, J. A. de Gouw, V. M. Bierbaum, and S. R. Leone, "Mobilities of aromatic ions drifting in helium," J. Phys. Chem. **100**, 14908 (1996).

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M. Krishnamurthy, J. A. de Gouw, L. N. Ding, V. M. Bierbaum, and S. R. Leone, "Mobility and formation kinetics of $NH_4^+(NH_3)_n$ cluster ions (n=0-3) in helium and helium/ammonia mixtures," J. Chem. Phys. **106**, 530 (1996).

E. B. Anthony, W. Schade, M. J. Bastian, V. M. Bierbaum, S. R. Leone, "Laser probing of velocity-subgroup dependent rotational alignment of N_2^+ drifted in He," J. Chem. Phys. **106**, 5413 (1997).

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M. Krishnamurthy, V. M. Bierbaum, and S. R. Leone, "Vibrational state dependence of the N_2^+ (v=0-3) + HCl reaction at thermal energies," Chem. Phys. Lett. **281**, 49 (1997).

M. J. Frost, S. Kato, V. M. Bierbaum, S. R. Leone, "Reactions of $N_2^+(v)$ with CO and NO," Chem. Phys., Special Issue on New Aspects of Photochemistry and Reaction Dynamics, **231**, 145 (1998).

S. Kato, V. M. Bierbaum, and S. R. Leone, "Multiquantum vibrational deactivation of $N_2^+(v)$ by collisions with N_2 and O_2 at thermal energies," J. Phys. Chem. A **102**, 6659 (1998).

J. Li, V. M. Bierbaum, and S. R. Leone, "Laser ionization time-of-flight mass spectrometer detection of methyl radical produced by ion reactions in a flowing-afterglow apparatus," Chem. Phys. Lett. **313**, 76 (1999).

L. Nugent-Glandorf, M. Scheer, M. Krishnamurthy, J. W. Odom, and S. R. Leone, "Photoelectron spectroscopic determination of the energy bandwidths of high harmonics (9th-55th) produced by an ultrafast laser in neon," Phys. Rev. A **62**, 023812-1 (2000).

E. B. Anthony, M. J. Bastian, V. M. Bierbaum, and S. R. Leone, "Laser probing of rotational state-dependent velocity distributions of $N_2^+(v"=0,J)$ drifted in He," J. Chem. Phys. **112**, 10269 (2000).

J. Li, V. M. Bierbaum and S. R. Leone, "Laser-induced fluorescence study of two weak vibrational bands of the O_2^+ $A^2\Pi_u$-$X^2\Pi_g$ system," Chem. Phys. Lett. **330**, 331 (2000).

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Personnel involved in the Research Effort

Stephen R. Leone, Principal Investigator

Veronica M. Bierbaum, Co-Principal Investigator

L. Nugent-Glandorf, Graduate Student, Ph. D. expected 2001

David Samuels, Graduate Student, 2000-present

Eric B. Anthony, Graduate Student, Ph. D. 1998.

Michael Scheer, Posdoctoral Research Associate, 1998-2000

Jian Li, Posdoctoral Research Associate, 1998-2000

M. Krishnamurthy, Posdoctoral Research Associate, 1995-1998

Shuji Kato, Senior Research Associate, University of Colorado, no cost to project, 1997-1999

Joost deGouw, Posdoctoral Research Associate, 1994-1996

Prof. Ed Grant, Department of Chemistry, Purdue University, Visiting Fellow, 1999-2000

Dr. Xueming Yang, Institute for Atomic and Molecular Sciences, Taiwan, Visiting Fellow, 2000

Thesis resulting from this Research Effort

Eric B. Anthony, Graduate Student, Ph. D. 1998, University of Colorado, "Laser probing of transport properties and rotational alignment of N_2^+ drifted in He," thesis available from the University of Colorado.

II. Summary of Research
A. Transport Properties of Atmospheric Ions

The mobility, diffusion, and velocity distributions of ions in gaseous media have been the subjects of intense theoretical and experimental investigation for many years.[33] Much of this interest arises from the need to obtain a better understanding of the transport of ions in discharges, lasers, semiconductor plasma processing, and various phenomena in the earth's atmosphere. Using flow tube techniques and arrival time measurements, we have determined the mobilities of aromatic ions[24] and of many atmospheric cluster ions.[21-23] Using Doppler resolved laser-induced fluorescence, we have examined the velocity distributions and molecular alignment of ions in drift fields.[17-20] In this last funding period, we have completed (1) an experimental and theoretical study of the mobilities of several cluster ions drifting in helium and in nitrogen,[26] (2) measurement of the rotational-state-dependent velocity distributions of N_2^+ drifted in helium,[27] and (3) detailed characterization of the alignment of N_2^+ in helium.[28]

1. Mobilities of Cluster Ions

Cluster ions of the type $A^+(B)_n$ where A^+ is a core ion (NO^+, H_3O^+) and B is a solvating molecule (H_2O, CH_3CN) are among the most abundant ions in the lower ionosphere of the Earth.[34,35] Although the formation kinetics have been studied, the mobilities are largely unknown. Using the selected ion flow-drift tube (SIFDT) apparatus, we have determined the mobilities of several atmospheric cluster ions through arrival time measurements. Core ions are produced in a low-pressure electron-impact ion source, mass selected using a quadrupole mass spectrometer, and injected into a flow tube where addition of the ligand molecule forms the cluster ions. The density of ions is momentarily depleted at two points in the drift tube by changing the electric field at those locations. At the downstream detection quadrupole, a multi-channel scaler records two minima in the otherwise constant mass spectrum pertaining to a specific cluster ion. The arrival-time difference yields the flight time between the two points, from which the drift velocity and mobility are obtained. These results[26] are quantitatively explained using the hard-sphere collision model by von Helden et al.[36] The role of ion-induced dipole interactions is investigated and shown to be minor for the mobilities of all but the smallest ions in helium. The existing data on cluster-ion mobilities in N_2, including the result here, are systematized. As a result of the greater polarizability of N_2, the hard-sphere collision model does not agree with the data, and a better explanation is obtained using a simple model that includes ion-induced dipole interactions. The remaining

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discrepancies between the measured and calculated results are attributed to ion-quadrupole or dipole induced-dipole interactions.

2. Rotational State Dependent Velocity Distributions of N_2^+

We have coupled single-frequency laser-induced fluorescence detection with our flow-drift apparatus to measure rotational state-resolved velocity component distribution functions of $N_2^+(v"=0)$ and thereby explore transport phenomena in unprecedented detail.[27] A trace amount of N_2^+ is drifted in helium as a buffer gas; the external axial electric field of the drift tube varies the center-of-mass collision energy of the ion-neutral pair. The net effect over hundreds of buffer gas collisions is to establish a steady-state anisotropic ion velocity distribution, the precise character of which is determined by the ion-neutral interaction potential, mass ratio, and field strength. A single-frequency ring dye laser is used to probe Doppler profiles of various rotational lines in the R-branch of the $(v',v") = (0,0)$ band of the B $^2\Sigma_u^+$ - X $^2\Sigma_g^+$ system at 390 nm, with the laser propagation direction set either parallel or perpendicular to the drift field. A small (3%) but definite increase in ion mobility with increasing rotational state from J=13.5 to J=22.5 is observed at a fixed field strength of 12 Td. Mobilities of J=15.5 measured over the range of 1.5 to 16 Td yield a $K_0(0)$ = 22.0 cm^2 V^{-1} s^{-1} and are in good agreement with earlier arrival-time measurements. These studies suggest that previous mobility values[37] for CO$^+$ in helium, which were determined by laser-induced fluorescence and showed disagreement with arrival-time results, are likely to be in error because of space-charge effects. Parallel translational temperatures of N_2^+ are found to be significantly higher than perpendicular temperatures; a difference of at least 140 K between these temperatures is measured for J=15.5 at 16 Td. No discernible difference between the parallel translational temperature for different rotational states is observed. There is evidence for a small degree of asymmetry or positive skewness (third central moment) in the parallel velocity component distributions; this is the first observation of a high velocity tail in a molecular ion-atomic buffer system.

3. Rotational Alignment of N_2^+

We have probed the rotational alignment of N_2^+ ions drifted in helium as a function of one component of sub-Doppler laboratory velocity by employing polarized laser-induced fluorescence.[28] By exciting with linearly polarized light and measuring the degree of polarization of the resulting fluorescence, the collision-induced quadrupole rotational alignment parameter $A_0^{(2)}$ is determined as a function of field strength and velocity subgroup. A strong correlation is found between the degree of rotational alignment and the velocity subgroup when probed parallel to the

field direction, with the alignment parameters generally increasing monotonically across the distribution. A dramatic difference in velocity-selected alignment as a function of rotational state is observed as well, for experiments conducted on various rotational lines at a fixed field strength of 12 Td. For sufficiently low rotational state (J about 9), it appears that $A_0^{(2)}$ changes sign across the Doppler profile.

B. Reaction Dynamics of $N_2^+(v)$

Vibrationally excited ions are important reactive intermediates in a number of environments including planetary atmospheres.[38,39] With AFOSR support, we have explored[12-16] the chemical reactions and deactivation processes for the vibrationally excited molecular nitrogen cation, $N_2^+(v)$, which plays an important role in the earth's atmosphere. During the last grant period we have extended our studies to include (1) the reaction of $N_2^+(v=0-3)$ with HCl,[29] (2) the reactions of $N_2^+(v)$ with CO and NO[30] and (3) the multiquantum vibrational deactivation of this cation.[31]

1. Reaction of $N_2^+(v=0-3)$ with HCl

Vibrationally excited nitrogen ions are formed by electron impact, mass-selected with a quadrupole mass filter, and injected into a reaction flow tube where they are allowed to react with hydrogen chloride. An excimer pumped dye laser, operating at 100 Hz is tuned to a suitable excitation wavelength to pump the molecular ions from a specific vibrational state v of the ground electronic state X $^2\Sigma_g^+$ to the excited electronic state B $^2\Sigma_u^+$. The fluorescence resulting from the B-X transition is collected onto a photomultiplier tube through a suitable bandpass interference filter. The decrease in the LIF signal of each vibrational state is measured as a function of the HCl flow to determine rate constants, and a second quadrupole mass filter is employed to determine the ion product branching ratios.

The reaction of N_2^+ with HCl is especially interesting since it proceeds by both charge transfer and hydrogen atom abstraction. We have found that the rate constants and product branching ratios for the reaction show little or no dependence on vibrational excitation of the reactant ion, and the rate constants for v = 0, 1, 2, and 3 are 5.3 (±1.6) x 10^{-10}, 8.3 (±2.5) x 10^{-10}, 7.9 (±2.4) x 10^{-10}, and 8.0 (±2.4) x 10^{-10} cm^3 molecule^{-1} s^{-1}, respectively. In addition, vibrational deactivation of the N_2^+ molecular ion is not significant, representing at most 20% of the total removal rate. The results are understood by a model in which an ion-molecule complex is formed at the collision rate, and there is only weak coupling of the vibrational excitation into the collision complex bond.

2. Reaction of $N_2^+(v)$ with CO and NO

The charge transfer reactions of N_2^+ with CO and NO have both fundamental and practical importance. The first of these reactions occurs in the inner coma of comets and interstellar and planetary media,[40] while the second occurs in the earth's atmosphere at altitudes of ~150 km where the nitric oxide concentration[41] is 10^7 molecule cm^{-3}. We have employed the selected ion flow tube-laser induced fluorescence technique for vibrational state specific measurements of the total removal rate constants and vibrational relaxation for reactions of $N_2^+(v)$ with CO and NO. Figure 1 shows the measured decay of the fluorescence signal as a function of reactant flow. For the $N_2^+(v=0)$ data, argon has been added to selectively remove higher vibrational states. Analysis of these data indicate that the removal rate constants for $N_2^+(v=0$ and 2) in collisions with CO are 0.76 (± 0.10) and 1.8 (± 0.3) x 10^{-10} cm^3 molecule^{-1} s^{-1}, respectively, obtained by comparison with the rate constant for the $N_2^+(v=1)$ + Ar charge transfer reaction. The increased reactivity with vibrational excitation arises both from vibrational deactivation and enhanced charge transfer. For $N_2^+(v=0$ and 2) in collisions with NO, the ions are removed with rate constants of 3.8 (± 0.3) and 6.3 (± 1.0) x 10^{-10} cm^3 molecule^{-1} s^{-1}, respectively. The increased reactivity with vibrational excitation arises primarily from vibrational deactivation. The high efficiency of this process is due to the long lifetime of the energized adducts.
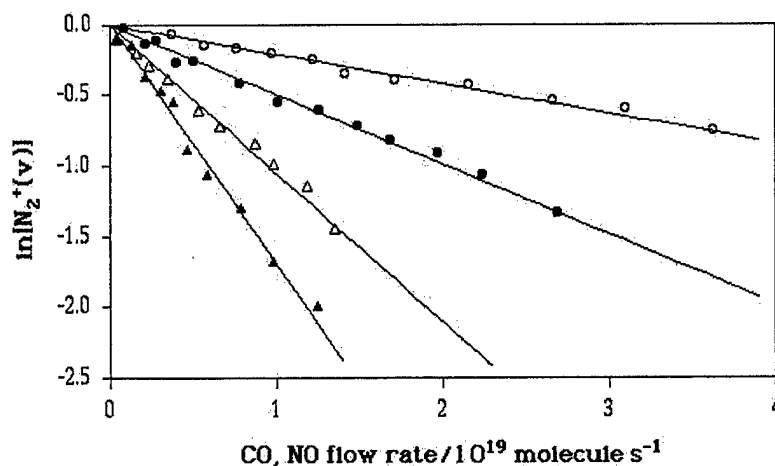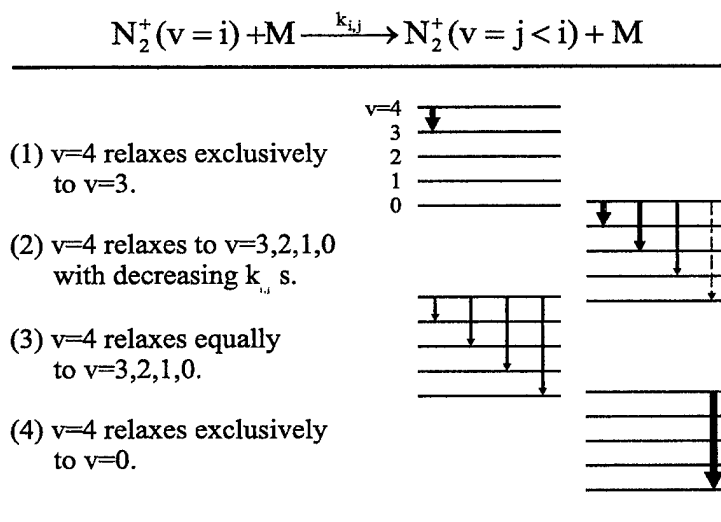

Figure 1. Semi-logarithmic plot of observed $N_2^+(v=0$ and 2) concentrations vs. reactant flow rate for $N_2^+(v=0)$ with CO (open circles) and NO (open triangles), and $N_2^+(v=2)$ with CO (closed circles) and NO (closed triangles).

3. Multiquantum Vibrational Deactivation of $N_2^+(v)$ by Collisions with N_2 and O_2

In the earth's atmosphere, the kinetics and dynamics of $N_2^+(v)$ are dominated by collision with molecular nitrogen and molecular oxygen. We have completed a comprehensive examination of the competition between charge transfer and vibrational deactivation in these reactions by employing the SIFT-LIF technique. Kinetic plots are measured for the intensity of fluorescence for $N_2^+(v=0,1,2,3,4)$ as a function of nitrogen and oxygen flow rates. These data are then analyzed using several models for vibrational relaxation as summarized in Figure 2. State-specific rate constants for the individual components of charge transfer and vibrational deactivation are determined from best fits to the data. The total rates of removal as a function of vibrational excitation are shown in Figure 3. The $^{15}N_2^+(v=0) + {^{14}N_2}$ reaction proceeds via symmetric charge transfer at one-half the Langevin rate constant ($0.5\ k_L$), indicating efficient charge equilibration, whereas the total removal rates of v=1-4 ($\sim 6 \times 10^{-10}\ cm^3$ molecule^{-1} s^{-1}) exceed $0.5\ k_L$. This indicates that vibrational transfer, in addition to charge equilibration, contributes to the removal of $N_2^+(v>0)$ by collisions with N_2. The $N_2^+(v) + O_2$ removal rates are significantly enhanced upon vibrational excitation; the total rate constant for v=4 is $3.0 \times 10^{-10}\ cm^3$ molecule^{-1} s^{-1}, six times larger than that for v=0. The enhancement is shown to be primarily due to increased vibrational

$$N_2^+(v = i) + M \xrightarrow{\ k_{i,j}\ } N_2^+(v = j < i) + M$$

(1) v=4 relaxes exclusively to v=3.

(2) v=4 relaxes to v=3,2,1,0 with decreasing $k_{i,j}$ s.

(3) v=4 relaxes equally to v=3,2,1,0.

(4) v=4 relaxes exclusively to v=0.

Figure 2. Models for $N_2^+(v)$ vibrational relaxation upon a single collision with reactant M. Relaxation of v=4 is schematically shown; the thickness of the arrows represents the relative magnitudes of k_{ij}.

deactivation, although a small enhancement of the charge-transfer channel also occurs for $N_2^+(v \geq 2)$ + O_2. Multiquantum vibrational energy transfer during single collisions plays an important role in the deactivation of $N_2^+(v \geq 2)$ with both N_2 and O_2. The occurrence of multiquantum deactivation is rationalized by the existence of significantly deep potential wells for N_2^+-N_2 and N_2^+-O_2 which arise from electron-exchange interactions.
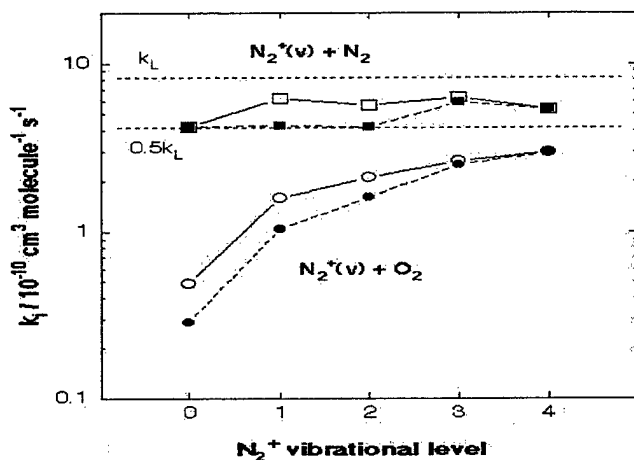

Figure 3. Total rates of removal for $N_2^+(v)$ as a function of vibrational excitation. Single-exponential fits to the LIF kinetic plots give raw rates (closed symbols). The actual rates for total loss, after correction for vibrational relaxation, obtained from the best fits are shown by the open symbols.

C. Detection of Methyl Radical Produced by Ion-Molecule Reactions

Radicals are of great importance in fuel combustion chemistry, since the oxidation of hydrocarbons is a chain-reaction process involving free radicals. The most difficult step in this process is thought to be chain initiation, i.e., the formation of radicals. To accelerate ignition processes, it has been proposed that ion-molecule reactions can be used to form the critical radicals[42] because ion-molecule reactions are typically 100 times faster than conventional combustion reactions between neutral molecules.

Scientists at the Air Force Research Laboratory have recently undertaken a comprehensive experimental study of the reactions of ions that might typically be found in ionized air with a variety of alkanes and aromatic compounds, especially those commonly found in fuels.[42-47] In these studies either a flowing-afterglow or a selected-ion flow tube is used. Their results show a remarkable degree of fragmentation of the product ions, both by the direct ionization process and by subsequent thermal dissociation due to the high exothermicity of these reactions. However, the

neutral-radical products formed in these reactions have not been studied. The neutral radicals will propagate the chain combustion and thus need to be identified for a full understanding of the combustion mechanism.

The conventional way of obtaining information about the neutral products from ion-molecule reactions is generally to deduce their identity from the product ions, since it is straight-forward to identify the ion products by means of various ion detection schemes or mass spectrometry, supplemented by a thermodynamic analysis. However, identification of the product ions does not always determine the identity and structure of the neutral products because of the high exo-thermicity of these ion-molecule reactions. Direct detection of neutral products from ion-molecule reactions in a flowing-afterglow apparatus would be very beneficial but is a challenging task.

With AFOSR support we have developed a novel method for the direct detection of neutral radicals. We have coupled a laser ionization scheme and time-of-flight (TOF) mass spectrometer detection with a flowing-afterglow instrument for the first time to directly detect methyl radicals that are produced from the reaction of CO^+ and N_2O^+ with methane.

1. New Instrumentation

A schematic of the new experimental apparatus for the detection of neutral radical products from ion-molecule reactions is shown in Figure 4.

In this new instrument reactant ions are formed by Penning ionization and electron impact on appropriate precursors in a stream of helium carrier gas. The neutral reactant is introduced into the flow tube through a ring inlet ~25 cm downstream of the ion source and ~20 cm before the laser detection region. Although the ion-molecule reactions have several products and subsequent reactions, we selectively detect the methyl radical product by laser ionization immediately before the sampling orifice. Production of 118 nm light (10.5 eV) by four-wave mixing is accomplished by focusing the 3rd harmonic of a Nd:YAG laser (50 Hz with a typical 355 nm output energy of 40-60 mJ per pulse) with a 35 cm focal length, fused-silica lens into a cell filled with Xe to a pressure of ~3.5 Torr. Both the 118 nm light and the excess 355 nm laser light intersect the gas flow perpendicularly and then illuminate a platinum plate at the other side of the chamber. A LiF lens (25 cm focal length at 200 nm) mounted inside the cell collimates the 118 nm light. Because of the difference in the index of refraction of LiF at 118 nm versus 355 nm, the 355 nm light diverges as it enters the chamber while the 118 nm light is collimated by the lens system. By removing the Xe from the tripling cell, we can determine the laser ionization effect associated with only the 118 nm

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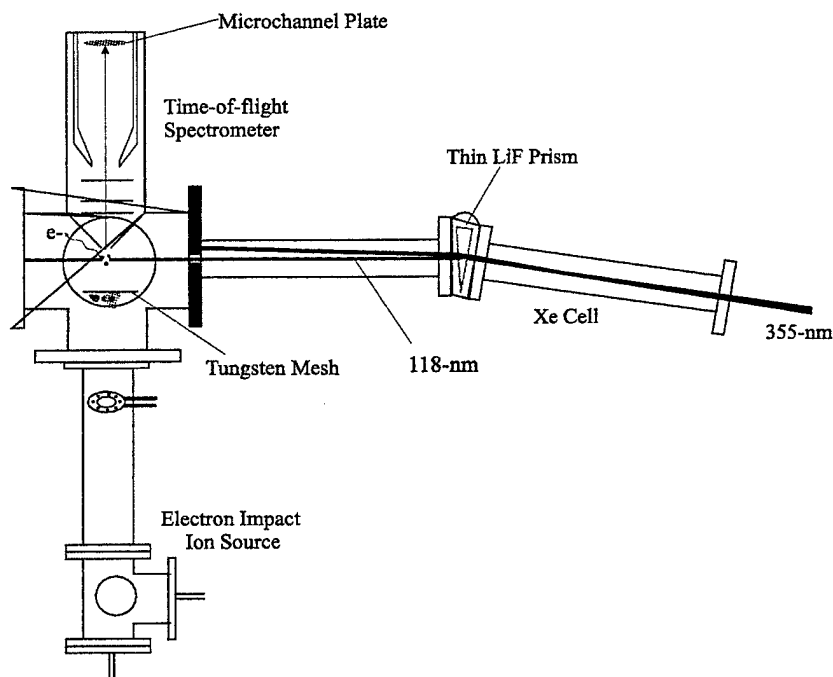
Figure 4. Schematic diagram of the new instrument which couples a flowing afterglow source with single photon ionization and time-of-flight mass spectrometric detection. The tungsten mesh depletes reactant and product ions and the LiF prism separates the 118 nm light from the intense background 355 nm light.

beam by subtraction. The relative intensity of the 118 nm beam is obtained by the photoelectron signal from the platinum plate.
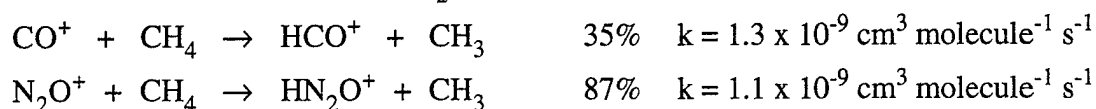
A small fraction of the reactants and products in the tube that are irradiated by the laser pass through the sampling orifice and enter the TOF spectrometer, which mass analyzes the reactant and product ions, as well as ions formed by laser ionization. The standard quadrupole mass spectrometer was replaced with the TOF spectrometer (designed in collaboration with R. M. Jordan Co.) because it provides more sensitivity (high collection for single-ion detection), wider mass range, and better mass resolution. Ions are detected by dual multi-channel plates and the output is monitored with both a digital oscilloscope and a multi-channel scaler. The TOF spectra are recorded after accumulating ion counts for 200 s. In order to distinguish the possible interference from photodissociation of parent ions with the laser-produced ions, in some experiments we added a double mesh to the end of the flow tube, placed about 1.5 cm upstream of the nose cone. A pulsed or DC voltage is applied to the mesh to partially block the parent ions.

The yield of the laser-ionized products is obtained by comparing mass spectra recorded with and without the 118 nm ionization laser (355 nm laser still on). The initial TOF spectra, which reflect the composition of the ions in the flow tube before laser ionization, are recorded without the

ionization laser. The TOF spectra are calibrated by assigning the known ions and then converting the counts versus arrival time into mass spectra.

2. Reactions of CO^+ with CH_4 and N_2O^+ with CH_4

The new experimental apparatus combining single photon laser ionization at 118 nm and time-of-flight mass analysis was utilized in initial experiments to directly detect methyl radicals that are produced from reaction of CO^+ and N_2O^+ with methane.

$$CO^+ + CH_4 \rightarrow HCO^+ + CH_3 \qquad 35\% \quad k = 1.3 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$N_2O^+ + CH_4 \rightarrow HN_2O^+ + CH_3 \qquad 87\% \quad k = 1.1 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

These systems were chosen for our initial studies because of the relative ease of ion generation from the parent compounds, the large reaction rate constants,[48,49] and the expected high yields of methyl radical. Preliminary studies led to several important instrumental improvements which were described above. In particular, the thin LiF prism was incorporated in the Xe tripling cell to reduce the intense 355 nm background light and thereby prevent multiphoton processes. In addition, the double mesh was added immediately before the laser ionization region to block reactant and product ions from the flow tube. In the absence of this mesh, photodissociation of CH_5^+ (formed by secondary ion-molecule reactions) was contributing to the observed signal of CH_3^+.

Figure 5 shows a narrow region of the time-of-flight mass spectrum for the detection of methyl radical. The dashed and solid lines show data in the absence and in the presence of laser ionization, respectively, Although the signal intensities are small, these results clearly show the production of radicals from the reactions of CO^+ and N_2O^+ with CH_4.

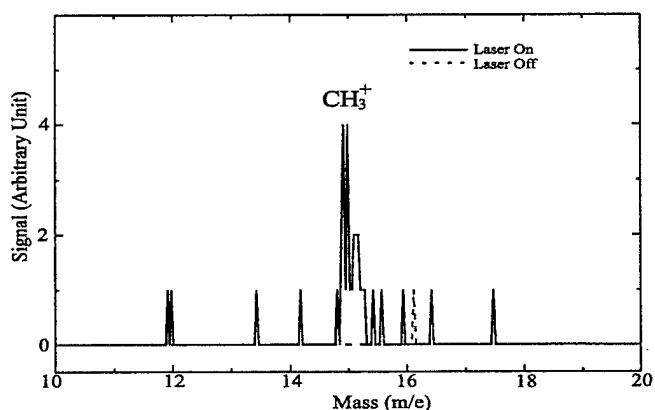**Figure 5.** Mass spectrum produced by single photon ionization at 118 nm of the methyl radical product of the $CO^+ + CH_4$ reaction.

III. References

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14. ABSTRACT
This research has focused on systems with particular relevance to atmospheric chemistry and combustion processes. In particular, the mobilities of cluster ions drifting in helium and in nitrogen buffer gas have been measured and the rotational state dependent velocity distributions and rotational alignment of the molecular nitrogen cation have been characterized. The reaction dynamics of the vibrationally excited nitrogen cation have been probed for reactions with hydrogen chloride, carbon monoxide, and nitric oxide and the multiquantum vibrational deactivation of this cation by molecular nitrogen and oxygen has been characterized. In addition, a new instrument was developed and the methyl radical products from the reactions of the parent cations of carbon monoxide and nitrous oxide with methane were detected for the first time.

15. SUBJECT TERMS
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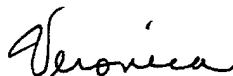Arlington, VA 22203-1977

Dear Mike:

Enclosed are the original and 2 copies of the Final Report for our AFOSR grant entitled "Ion Dynamics Related to Hypersonics"(#F49620-98-1-0113). We look forward to hearing from you about the possible renewed funding of this program.

Sincerely yours,

Stephen R. Leone
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